Ionic liquid doped polybenzimidazole membranes for high temperature Proton Exchange Membrane fuel cell applications

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HIGHLIGHTS

► PBI porous support filled with proton conductive support.
► PBI porous membrane properties tailored for the application.
► PBI/IL outperforms Nafion 117 at elevated temperatures.

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ABSTRACT

In this work we propose the use of the ionic liquid 1-H-3-methylimidazolium bis(tri-fluoromethanesulfonyl)imide ([h-mim] Ntf2) as conductive filler in a tailor-made porous, polymeric polybenzimidazole (PBI) support as proton conductive membrane for high temperature (>100 °C) fuel cell applications. PBI is chosen because of its excellent thermal and mechanical stability, while the choice for the ionic liquid is based on its high proton conductivity, low water sorption, thermal stability and low viscosity.

The morphology of the porous PBI support is especially tailored for this application using a delayed immersion precipitation process. The macrovoid free porous structure has a volume porosity of 65% and a pore size of approximately 0.5 μm.

Pores filling with ionic liquid by direct immersion of the PBI support into molten ionic liquid at 50 °C introduced the membrane proton conductivity. After impregnation the proton conductivity of this PBI/IL membrane reached a value of 1.86 mS cm^{-1} at 190 °C. Fuel cell performance of these membranes clearly exceeds that of Nafion 117 at temperatures above 90 °C. A power density of 0.039 W cm^{-2} is obtained at the intended operation temperature of 150 °C, which proofs that the developed PBI/IL membrane can be considered as a serious candidate for high temperature fuel cell applications.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) receive great interest as an alternative sustainable energy source, because the availability of traditional fuels such as oil and natural gas becomes more exhausted. Also the need for less environmental constraining energy sources gets more essential.

In the past decades, PEMFCs have been successfully developed for operation at temperatures below 100 °C [1]. There are, however, disadvantages linked to these relative low operational temperatures

[2]. An expensive platinum catalyst is needed to obtain sufficiently high reaction rates [2,3]. A high sensitivity for fuel impurities like CO, and low value waste heat are other critical issues [2,4,5].

In contrast, PEMFCs operating at higher temperatures for application in e.g. the automotive industry have a number of benefits. The reaction rate at both electrodes is increased. A better CO tolerance allows a simplified fuel pretreatment [2,5,6], and a higher operating voltage can be obtained. Cogeneration of heat and power production becomes possible [7].

Perfluoride-based membranes such as Nafion® are available for PEMFCs [2,5,8–10]. However its application in high temperature fuel cells is only limited as Nafion® membranes show proton conductivity at elevated humidity levels only, limiting its use to temperatures below 100 °C. The development of membranes and

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fuel cell devices for high temperature applications under dry conditions is rather ambitious [2]. Current directions of such membrane development can be predominantly classified according to membranes based on: 1) modified Nafion® composite membranes, 2) functionalized non-fluorinated membranes and 3) acid-base composite membranes [2].

Recently, Park et al. [11] reviewed the efforts performed in developing sulfonated hydrocarbon proton exchange membranes for application in medium temperature and/or low humidity fuel cells as alternative for the use of Nafion®. Focus is mainly on mimicking the architecture of Nafion and to create so-called effective water channels using multiblock copolymers, highly sulfonated polymers with aromatic and/or aliphatic side chains or high free volume polymers [11]. The authors concluded that, despite the progress made, the current membrane targets for practical application are still challenging.

Research on membrane development for sustainable high temperature PEMFCs operating under water free, dry conditions is frequently directed towards dense polybenzimidazole (PBI, poly(1,4-phenylene-5,5 (6-bibenzimidazole-2,2—diyl))) membranes. PBI is an excellent candidate for use in a high temperature environment [12]. It has excellent chemical and thermal stability [13], and it is often used in thermal protective clothing and fire blocking applications [12]. Depending on its grade, PBI has an upper working temperature between 260 °C and 400 °C [12]. The repeating unit of PBI is given in Fig. 1.

As most polymers, also PBI is an electrical insulator and many attempts have been made in recent years to improve the proton conductivity of polymers and more specifically PBI for PEMFC applications. Lee and Kerres [14] characterized several polymer blends of PBI and sulfonated poly(arylene thioether)s and these membranes showed a proton conductivity of 120—220 S cm^{-1} at room temperature. Often, PBI is doped with phosphoric acid to promote proton conductivity. Lobato et al. [15] studied the influence of the H_3PO_4 doping content on the proton conductivity of dense PBI membranes prepared by solvent evaporation after casting. The doping level was varied between 3.1 and 6.2 mol of H_3PO_4 per mol PBI. They report a maximum value of 15 mS cm^{-1} for anhydrous membranes and a maximum value of 39 mS cm^{-1} after equilibration of the membrane in humid air at 190 °C.

Alternatively Carollo et al. [16] used different types of PBI polymer backbones to study the effect on phosphoric acid dope capability and resulting proton conductivities. ABPBI (poly(2,5-benzimidazole)) was compared to two naphthalene based PBIs and a pyridine based PBI. Dense films were prepared by evaporation of the solvent from the polymer solution. After that the films were dried and soaked in H_3PO_4 solutions. The highest proton conductivity measured exceeded 100 mS cm^{-1} at 80 °C at a RH of 40% in the case of the pyridine based PBI.

Recently, Shen et al. [17] synthesized a new sulfonated organic acid, 1H-imidazole-4-sulfonic acid and prepared hybrid, dense PBI membranes using this acid as ion conductive phase to further increase the degree of phosphoric acid doping. The conductivity of the hybrid membranes increased with both the temperature and

the acid content, while only slightly reducing the mechanical properties of the membranes. Yang et al. [18] used an alkyl imidazole functionalized polysulfone to further increase the degree of phosphoric acid doping. Although the synthesis route was rather complex, including chloromethylation followed by functionalization, an acid doping level of about 10—11 mol H_3PO_4 per mole of the imidazolium group could be obtained, resulting in proton conductive properties of 15—22 mS cm^{-1} at 130—150 °C at 15 mol% water vapor in air. Fuel cell characterization showed an open circuit voltage of 0.96 V and a peak power density of 175—204 mW under dry conditions at 150 °C.

Although the use of phosphoric acid introduces high proton conductivity, the presence of phosphoric acid has disadvantages regarding chemical stability (pyrolysis of phosphoric acid at 150 °C) and environmental issues [19]. The use of ionic liquids (ILs) as conductive fillers to replace phosphoric acid is proposed to overcome these disadvantages [7]. Ionic liquids (ILs) are purely ionic materials with a melting temperature often around room temperature. Ionic liquids have favorable properties regarding temperature stability such as non-volatility and non-flammability, and a rather high ionic conductivity [20]. The advantage of ILs over phosphoric acid is their excellent thermal stability at higher temperatures (>150 °C) and the more environmentally friendly character. Wang et al. [19] described the introduction of IL into a fluor containing dense PBI membrane. Neves et al. [21] modified Nafion by incorporating different degrees of ionic liquid cations in the dense membrane, which turned out to be a good method to tailor the properties of the final membranes towards the desired application. Ye et al. [22] report on PBI membranes loaded with anhydrous H_3PO_4 and the protic ionic liquid 1-propyl-3-methyl-imidazolium dihydrogen phosphate. They prepared this membrane by solvent evaporation from a PBI/H_3PO_4/ionic liquid solution, resulting in a dense membrane. The proton conductivity was increased with increasing doping level of the ionic liquid. A maximum conductivity of 2.04 mS cm^{-1} at 150 °C was found at completely anhydrous conditions. Mondal et al. [23] used the aprotic ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate (EMIES) to increase the proton conductive character of sulfonated poly(ether ether ketone) (SPEEK) membranes for use in fuel cells under dry conditions. The ionic interaction between SPEEK and EMIES resulted in the formation of homogeneous dense films. The prepared membrane exhibited a conductivity of 0.57 mS cm^{-1}, which increased significantly to 18.94 mS cm^{-1} at 150 °C under anhydrous conditions, due to the well-connected proton conducting channels formed in the polymer matrix because of good miscibility and interaction with EMIES.

So far, all these systems used dense membranes, with the conductive additive mixed with the polymer before membrane preparation. As an alternative, which allows tuning of the individual properties of both the conductive and the polymer matrix, Yamaguchi et al. [24] proposed the concept of a conductive filler embedded into a porous, polymeric matrix. They used a poly(vinylsulfonic acid/acrylic acid) crosslinked conductive gel in a porous polytetrafluoroethylene (PTFE) open polymeric support. This synergistic concept combines the mechanical strength of the support with the conductivity of the conductive gel. Lin et al. [25] used a porous poly(tetra fluorocarbon) (PTFE) support and impregnated this support with PBI using a coupling agent containing perfluorocarbon sulfonic acid ionomer. Due the low thickness of the resulting membrane (i.e. ∼22 μm), the impregnated PTFE membranes outperform the native PBI membranes which have a thickness of ∼100 μm.

To the best of our knowledge, the combination of a porous PBI support prepared by phase separation with tailored properties and filled with an IL for use in fuel cell applications has not been
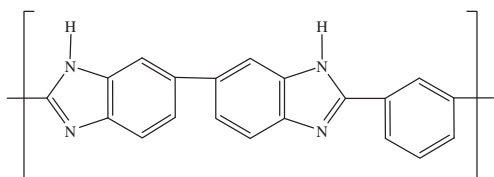

Fig. 1. Repeating unit of PBI (polybenzimidazole, poly(1,4-phenylene-5,5 (6-bibenzimidazole-2,2—diyl))).

reported in literature yet. Following this idea, here we propose the design and development of such a system, using the ionic liquid [h-mim] Ntf2 as the conductive filler in a porous, polymeric PBI matrix with tailored morphology as membrane for high temperature (>100 °C) fuel cell applications. PBI is chosen because of it excellent thermal and mechanical stability, while the choice for the ionic liquid is based on its high proton conductivity, thermal stability and low viscosity.

In this paper we report a method to prepare and tailor the properties of the porous PBI support and the preparation of the IL impregnated proton conductive PBI membrane. As both the support and the IL are tailor-made, it allowed optimization of the properties of both for the desired application. The synergistic combination of thermal and mechanical strength provided by the porous PBI support and the proton conductivity obtained from the IL unites the best properties of both materials. The performance of these membranes in high temperature fuel cell applications is evaluated in terms of proton conductivity and fuel cell power output and compared to that of Nafion® membranes.

2. Experimental

2.1. Materials

Polybenzimidazole (PBI) was kindly supplied by FumaTech GmbH, Germany.

[h-mim] Ntf2 (Fig. 2) was used as ionic liquid and kindly provided by Solvionic (France). Solvionic published on their website, http://en.solvionic.com, physical data of the selected ionic liquid. [h-mim] Ntf2 shows a proton conductivity of 7.2 mS cm^{-1} at room temperature, has a molar mass is 363.28 g mol^{-1}, a melting point of 30 °C and a decomposition temperature of 423 °C. The IL is not at all miscible with water, the water content of solid IL is<0.05 wt.%, which is equal to <0.03 mol l^{-1}. This property prevents instability effects, i.e. IL being pushed out of the porous PBI support by excessive water uptake.

Polyvinylpyrrolidone (PVP) with a M_w of 40 kDa type K30, type K90 with a M_w of 360 kDa and lithium chloride were purchased from Sigma−Aldrich GmbH (Germany). N-methyl pyrrolidone (NMP) 99% was purchased from Acros (Belgium). Ethanol and n-hexane (both analytical grade) were purchased from Merck (Germany). All materials were used as received. Ultrapure water was obtained from a Synergy water supplier from Millipore S.A.S. (France) equipped with a 0.22 μm filter from Millipore (USA).

2.2. PBI support preparation

A roundbottom flask, equipped with a 2-blade propeller stirrer, was placed into an oil bath, which was heated to and kept at 175 °C. The polymer solution was prepared by slowly adding 12 g of PBI powder and 2 g of LiCl to 82 g of NMP. LiCl was used to stabilize the

Fig. 2. Chemical structure of the ionic liquid 1-H-3-methylimidazolium bis(tri-fluoromethanesulfonyl)imide, [h-mim] Ntf2.

PBI solution [26]. After thoroughly mixing for 24 h, the solution was cooled down to room temperature and filtered over a 15 μm metal Bekipor filter type ST 15 AL 3 (Bekeart) to remove residual particles and agglomerates. The polymer solution was reheated to 175 °C and 2 g of PVP K30 and 2 g of PVP K90 powder were added under thoroughly stirring. Addition of PVP suppresses macrovoid formation upon demixing and improves the casting properties [27,28]. After cooling to room temperature a moderate viscous light brown polymer solution was obtained.

The PBI support was prepared by casting the polymer solution at room temperature on a clean glass plate using a casting knife with a thickness of 0.2 mm.

The glass plate with the cast polymer solution was immersed in an NMP/water (50/50) coagulation bath for 30 min. The optimal composition of the coagulation bath was determined by increasing the NMP concentration from 0 to 50 wt.% in consecutive casting experiments. The formed PBI support was immersed in pure water to rinse out the last traces of solvent. Subsequently the PBI support was immersed in ethanol for 30 min, followed by hexane for 30 min, to ensure complete removal of water. The PBI support was then placed between two glass plates spaced 1 mm apart and heated to 150 °C in an oven to remove all volatiles. Flat PBI supports were obtained.

2.3. Impregnation of IL into PBI support

The ionic liquid was heated to 50 °C in a Petri dish to melt the salt. The porous PBI support was submerged into the molten ionic liquid for 1 h. After that the Petri dish with membrane and molten IL was placed under vacuum for 10 min to remove air bubbles. Subsequently the membranes were removed out of the ionic liquid and the surplus of ionic liquid on the membrane surface was wiped off with a tissue.

2.4. SEM characterization

Cross sections of both the PBI support and the PBI/IL membranes were prepared. Samples were wetted with glycerol/water (10/90) and fractured in liquid nitrogen. The samples were gold coated using a Balzers Union SCD 040 sputter equipment operating at 210 V and 13 mA during 180 s in a 10 mbar argon atmosphere. SEM pictures were taken using a Jeol scanning electron microscope (JSM 5600LV) operating at 5 kV.

2.5. Volume porosity

A Micrometrics pycnometer model ACCUPYC 1330 was used to determine the volume porosity of the prepared PBI supports and the PBI/IL membranes. The measurement was based on Archimedes' displacement principle and the sample volume was determined by measuring the pressure change of helium in a calibrated volume. The method is described elsewhere [29]. For each experiment 10 samples were measured.

2.6. Thermal analyses

A Perkin Elmer TGA 7 system was used to determine the thermal behavior of the PBI and PBI/IL membranes. A 5−10 mg sample was investigated in the temperature range from 30 to 300 °C at a controlled heating rate of 20 °C/min under a nitrogen flow of 10 ml min^{-1}.

2.7. Proton conductivity

The proton conductivity measurements at ambient temperature were performed in a tailor-made cell [30]. The cell has a Teflon
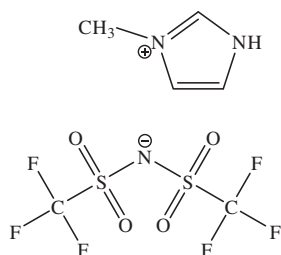
interior with two gold-coated stainless steel electrodes. Both electrodes were connected with two wires, one for the current and the second acting as potential probe [30]. Membrane samples of approx. 1 cm^2 were cut and sandwiched between the two electrodes having a surface area of 0.27 cm^2. The membrane thickness was 50 μm. The cell was connected to a PG stat with an integrated frequency response analyzer Autolab potentiostat (ECO-Chemie, The Netherlands). An alternating electrical field was supplied onto the membrane and the response was monitored.

To approach actual operating conditions, proton conductivity at high temperatures (150–190 °C) was measured as well. Approx. 1 cm^2 of membrane was clamped between two electrodes with a surface area of 0.64 cm^2. The assembly was placed in a temperature controlled tube oven. Impedance spectra were recorded using a PGstat20 Autolab Potentiostat with integrated frequency response analyzer (ECO-Chemie, The Netherlands) under a dry nitrogen flow (45 ml min^{-1}).

In both cases (low and high temperature), the voltage applied between the electrodes was 10 mV to ensure that linear measurements were performed. No predetermined voltage was applied. The frequency ranged from 100 Hz to 100 kHz. Measurements in the potentiostatic mode (single scan) were performed. The resistance value was determined from a Z (Imaginary) − Z (Real) plot using the high frequency intercept of the impedance with the real axis. The proton conductivity was calculated from:

$$\sigma = l/RA \qquad (1)$$

where σ is the proton conductivity in S cm^{-1}, l is the distance between the electrodes i.e. the membrane thickness in cm, R is the measured resistance in Ohm and A is the surface area of the electrodes in cm^2.

2.8. MEA assembly and fuel cell performance

MEAs with a membrane area of 6.25 cm^2 were assembled. A commercially available gas diffusion electrode type ELAT® loaded with 5.0 mg Pt cm^{-2} (BASF) was used at both sides of the membrane. The electrode-membrane-electrode stack was prepared by hot pressing at 50 kN and 150 °C during 3 min using a Fontijne hot press model THB 400 (Vlaardingen, The Netherlands).

The MEA fuel cell performance was evaluated using a H$_2$/O$_2$ fuel cell set up (ECN, the Netherlands). This set up consisted of two graphite blocks, attached to the anode and the cathode, in which a serpentine flow pattern was etched to supply the fuel gasses. Both graphite blocks were connected to an adjustable electrical load.

The MEA was clamped between the two graphite blocks. Dry hydrogen gas with a flow rate of 40 ml min^{-1} and a back pressure of 1.5 atm was supplied to the anode and dry oxygen gas with a flow rate of 70 ml min^{-1} and a back pressure of 1.5 atm was supplied to the cathode through the serpentine flow pattern.

Prior to the experiment, the MEA was pre-conditioned for each test temperature by operating the set up at 60 mV until a stabilized current was reached. The temperature was increased stepwise between the experiments while the MEA was kept in place. The steady state polarization curves of cell voltage versus current were recorded under galvanic control. A computer running on Nova 1.5 software was used for data acquisition.

3. Results and discussion

3.1. Preparation of porous PBI support

The porous PBI support is prepared by phase separation of the homogeneous polymer solution into a polymer rich and a polymer
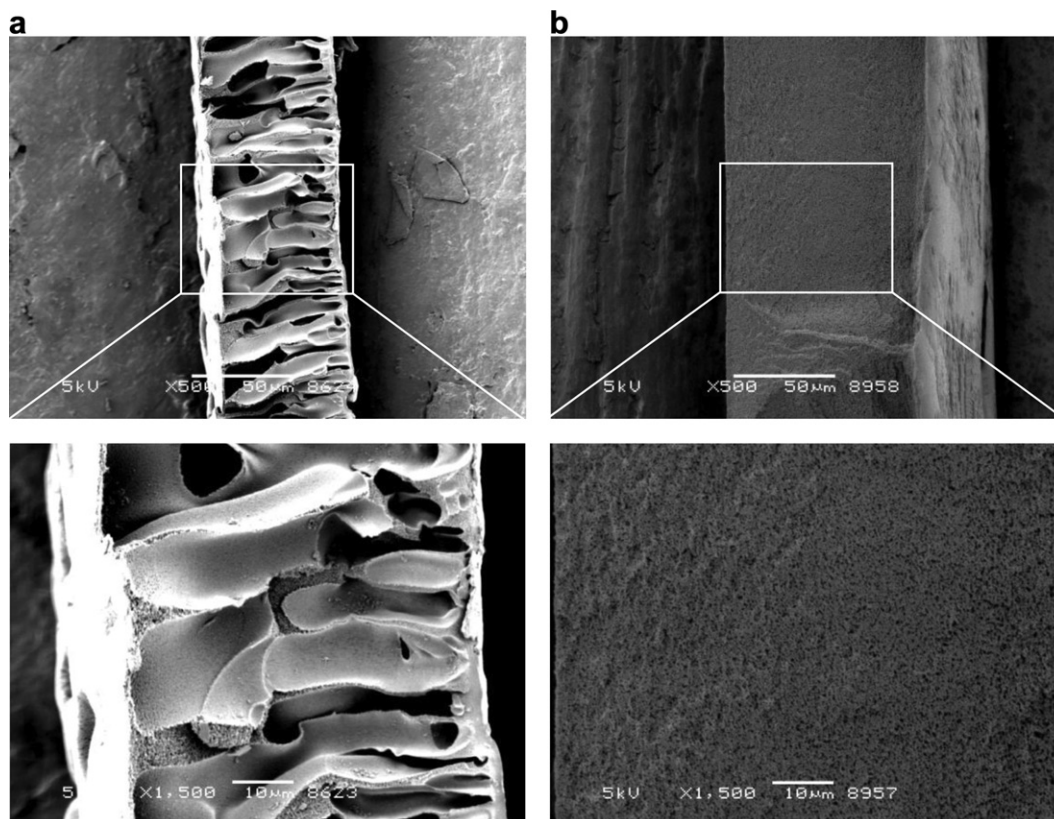

Fig. 3. PBI support structure after (a) rapid immersion precipitation in water and (b) delayed immersion precipitation in a mixture NMP/water 50/50 wt.%.

Table 1
Effect of coagulation bath composition on the PBI support structure.

Water/NMP (wt.%)	Macrovoids
100/0	Yes
90/10	Yes
80/20	Yes
70/30	Yes
60/40	Small
50/50	No

Fig. 5. Thermogravimetric curves of PBI (continuous line) and PBI/IL (dashed line).

lean phase. Depending on the coagulation bath used for phase inversion, two different ways of liquid–liquid demixing of the polymer solution can be distinguished at the onset of phase separation. The onset can coincide with the moment of contact between the polymer solution (film) and the non-solvent bath. This is the case when purely water is used as the non-solvent. In this case instantaneous demixing occurs. If the onset is delayed for a certain period due to the addition of solvent to the non-aqueous coagulation bath, delayed demixing occurs.

SEM pictures of the prepared porous PBI structures using water (a) or a mixture of water/NMP 50/50 wt.% (b) as coagulation bath are shown in Fig. 3. Distinctively different structures are obtained. The use of solely water as coagulant caused a rapid, instantaneous demixing, resulting in a porous structure with huge macrovoids (Fig. 3a). This is undesirable as macrovoid formation reduces the mechanical stability of the matrix and prevents a homogeneous distribution of the IL in the membrane. The addition of PVP to the polymer solution, which is frequently used in membrane development to suppress macrovoid formation, proofed to be insufficient to overcome this. As an alternative route to suppress macrovoids formation the addition of solvent (NMP) to the coagulation bath was evaluated. This slows down the phase separation process (delayed de-mixing), which results in suppression of the formation of macrovoids (Fig. 3b).

In order to determine the appropriate ratio of non-solvent (water)/solvent (NMP), a series of different experiments was performed using different water/NMP ratios. From each prepared PBI support, cross sections were investigated using SEM to evaluate the structure in terms of the existence of macrovoids. The results are summarized in Table 1.

The use of coagulation baths with 0–40 wt.% NMP results in macrovoid formation. The addition of more than 50 wt.% of NMP to the coagulation bath results in mechanically weak membranes. Therefore NMP/water 50/50 wt.% is considered as the most optimal composition for the coagulation bath to prepare macrovoid free, porous structures suitable for impregnation with the IL.
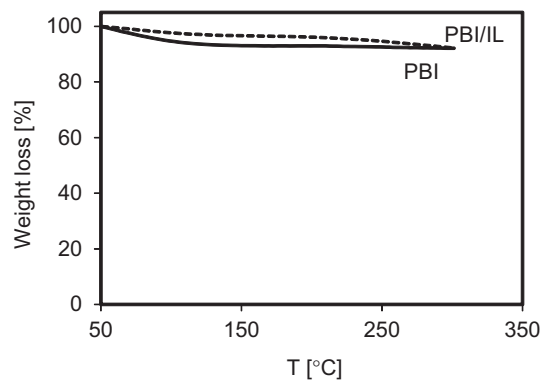
3.2. Membrane characterization

The prepared PBI support and PBI/IL membranes were characterized regarding volume porosity and extend of pore filling, thermal stability and proton conductivity for use in a high temperature PEM fuel cell.

The porous PBI support has a volume porosity of $65.6 \pm 2.8\%$, whereas PBI/IL shows a volume porosity of $36.6 \pm 5.3\%$. These data show a significant decrease in volume porosity of the PBI/IL membrane because of the impregnation of the porous support with the IL.

The effect of impregnation of the IL in the PBI support on the membrane morphology was investigated using SEM. Fig. 4 shows two representative pictures of the cross sections of a) the porous PBI and b) the PBI/IL membrane.

In the cross section of the neat PBI support (Fig. 4a), medium sized pores of approx. 0.5 μm can be distinguished. These are absent in the case of the IL impregnated membrane (Fig. 4b), which confirms that the pores of the porous PBI support are filled with IL.

The PBI/IL membranes are supposed to operate at temperatures in the range of 150–190 °C. TGA analysis of the PBI support and the PBI/IL membranes was performed (Fig. 5) and showed only a small weight loss between 150 and 300 °C.

For both membranes moisture loss is visible between 50 and 150 °C. This weight loss due to water evaporation is approx. 10%. Above 200 °C, the PBI/IL membrane shows a small additional weight loss of approx. 5%. We hypothesize this can be attributed to the ionic liquid. A small trace of 1-H-methyl imidazolium with a boiling point of 198 °C or bis(trifluoromethanesulfonyl)imide with a boiling point of 190.5 °C, which is used for IL synthesis may remain in the IL after synthesis and evaporation. Both membranes
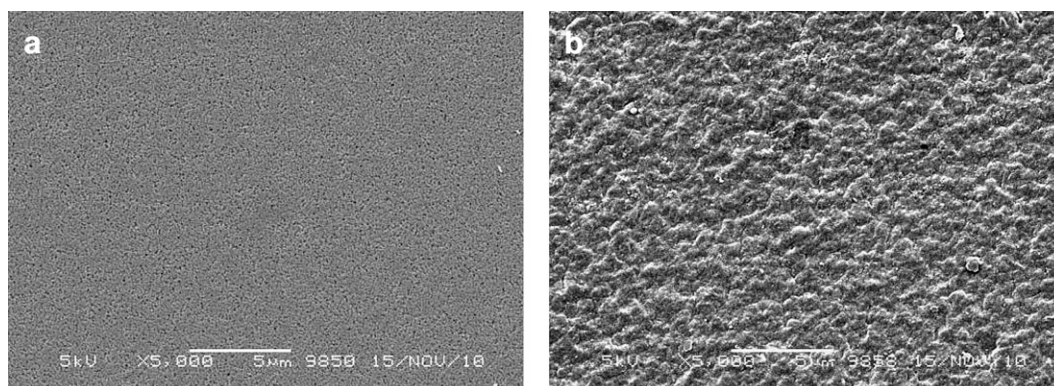

Fig. 4. Cross sections of a) neat PBI and b) IL impregnated PBI).

Table 2
High temperature proton conductivities for PBI/IL membranes.

Temperature (°C)	Proton conductivity (mS cm^{-1})
129	1.35 ± 0.04
162	1.53 ± 0.05
190	1.86 ± 0.06

are thermally stable in the intended operation temperature range of 150–190 °C.

The proton conductivity at room temperature and at elevated temperatures of the porous PBI support, the PBI/IL membranes and Nafion® 117 was determined. The values for Nafion® 117 were determined for comparison.

The proton conductivity of PBI and PBI/IL in the wet state has not been measured, as this is not relevant for fuel cell operation above 100 °C. In the dry state, the porous PBI support has a proton conductivity of 0.003 ± 0.002 mS cm^{-1} at room temperature, while the dry PBI/IL membranes show a proton conductivity of 0.5 ± 0.1 mS cm^{-1} at room temperature. At these temperatures, humidified Nafion® 117 outperforms the dry PBI/IL membranes. At room temperature, under humidified conditions, Nafion® 117 has a proton conductivity of 11.5 ± 1.5 mS cm^{-1}. In the dry state however, Nafion® 117 does not show any proton conductivity. When the materials in the dry state are compared, the PBI/IL membrane shows the highest proton conductivity.

As we aim at fuel cell operation at high temperatures, the proton conductivities of the PBI support and the PBI/IL membranes between 129 and 190 °C were determined as well. The results are summarized in Table 2.

The IL filled PBI membranes show a proton conductivity which is 250–450 times higher than the values obtained for the unfilled, native porous PBI support (0.003 mS cm^{-1} at 134 °C and 0.007 mS cm^{-1} at 190 °C). The proton conductivity of the PBI/IL membrane significantly increases with increasing temperature and reaches a value of 1.86 mS cm^{-1} at 190 °C.

At these temperatures all the moisture has been removed and the observed proton conductivity increase can be fully attributed to the IL in the PBI support. The results also prove that the PBI/IL membranes can withstand temperatures up to at least 190 °C without losing their conductive properties.

3.3. Fuel cell performance

Fig. 6 presents the results of the polarization curves for a) Nafion® 117 and b) the developed PBI/IL membranes at 30 °C, 60 °C, 90 °C, 120 °C and 150 °C under dry conditions (feed not humidified).
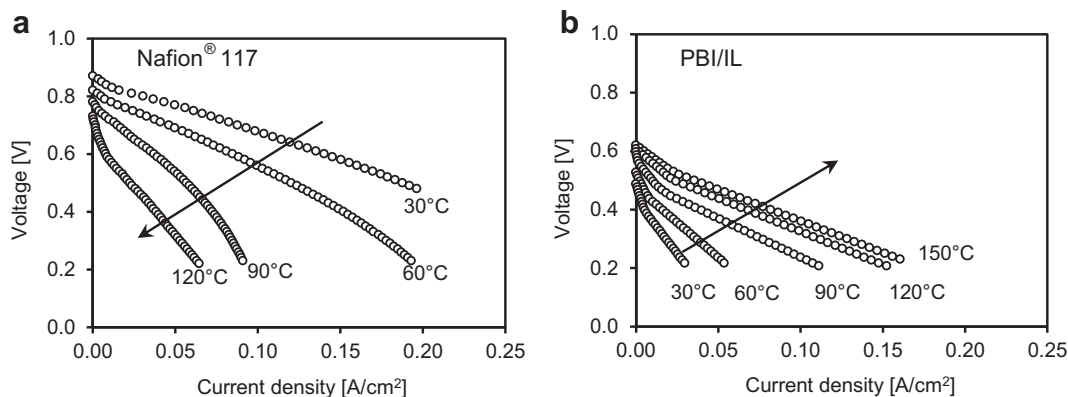
The performance of Nafion® 117 (Fig. 6a) obviously decreases with increasing operating temperature. The reason for this is that Nafion® 117 needs to be humidified for good operation, which can be maintained by e.g. humidification of the feed components. At higher temperatures the relative humidity decreases and consequently the performance of the Nafion® N117 MEA decreases. Fig. 6a shows that the OCV drops from 0.88 V at 30 °C to a value of only 0.70 V at 120 °C. An even more pronounced performance drop is observed at higher currents and temperatures. Polarization curves at 150 °C could not even be obtained due to the absence of moisture.

The developed PBI/IL membranes on the other hand show an enhanced performance, especially at higher temperatures. At low temperatures, an OCV of only 0.48 V is obtained. However it increases significantly to a value of 0.62 V when the operating temperature is increased to 150 °C. The performance of the PBI/IL membrane increases with increasing operating temperature due to the higher transport and reaction rates.

We hypothesize that the low OCV may be the consequence of the fact that the porous PBI support is not completely filled with the IL, as confirmed by the porosity measurements. The IL filling decreased the porosity from 65.6 to 36.6%. Since at the temperature of impregnation, the viscosity of heated IL is still relatively high, the smaller pores present in the support are most likely not completely filled with IL, resulting in a relatively low OCV value.

In addition, it could also originate from the membrane surface being less smooth reducing optimal contact between membrane and electrodes.

The superiority of PBI/IL over Nafion® 117 at temperatures above 100 °C becomes even more pronounced when the power density is considered (Fig. 7).

Fig. 7 clearly shows the superior performance of the PBI/IL membranes over Nafion® 117 at higher temperatures (especially when $T > 100$ °C). With increasing temperature, the fuel cell performance of Nafion® 117 decreases due to the reduction in relative humidity. In contrast to this, the fuel cell performance of the developed PBI/IL membranes increases with increasing operating temperature due to the increased proton transfer rate through the ionic liquid phase of the membrane. During the measurement, which last for approx. 4 h, the PBI/IL membrane performed well at the different temperatures. The low water uptake, which is a unique property of the selected IL, prevents IL being pushed out of the support by excessive water uptake.

Fig. 8 shows the power density of both the Nafion® N117 membrane and the developed PBI/IL membrane as a function of the temperature. The results clearly show the superior character of the PBI/IL membrane at higher temperatures.
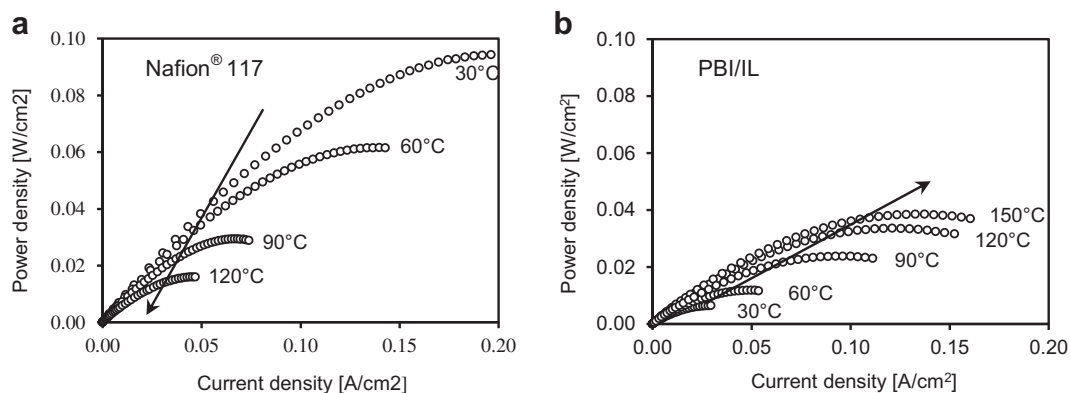

Fig. 6. H$_2$–O$_2$ polarization curves as a function of the operating temperature without humidification for a) Nafion® 117 and b) PBI/IL membranes. The arrows indicate the direction of increasing temperature.

Fig. 7. Power densities as a function of the operating temperature for a) Nafion® 117 and b) PBI/IL membranes. The arrows indicate the direction of increasing temperature.
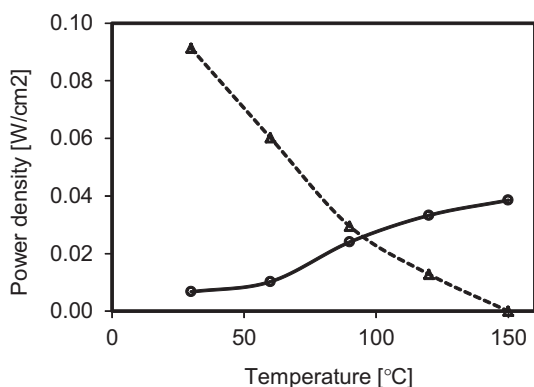

Fig. 8. Fuel cell performance as a function of the temperature for Nafion® 117 (▲) and the developed PBI/IL membranes (●).

At temperatures below approx. 95 °C, Nafion® 117 shows a better performance than the developed membrane. However, from 95 °C on, the power output obtained for the fuel cell with the PBI/IL membrane starts to exceed that of the fuel cell with Nafion® N117, resulting in a superior performance at the desired operating temperature of 100-150 °C. A power density of 0.039 W cm^{-2} is obtained at the intended operation temperature of 150 °C, which proofs that the developed PBI/IL can be considered as a serious candidate for high temperature fuel cell applications. Although the obtained conductivities and power outputs are still low compared to the work done on phosphoric acid doped PBI, this work shows the potential of the use of ionic liquids as green alternative to introduce proton conductivity. Further improvement is mainly foreseen in terms of the effectiveness of pore filling of the porous PBI support with the IL to reach complete filling of the pores and in optimization of the MEA preparation.

4. Conclusions

A PBI/IL proton conductive membrane for application in high temperature fuel cells has been developed. The morphology of the porous PBI support has been tailored to meet the desired requirements, resulting in a porosity of 65.6%. To introduce the ionic conductivity, the non-conductive porous PBI support was filled with the ionic liquid H-3-methylimidazolium bis(trifluoromethanesulfonyl) imide ([h-mim] Ntf2). The resulting membrane shows a proton conductivity of 1.86 mS cm^{-1} at 190 °C whereas the PBI support has no conductivity, showing reasonable filling of the pores of the PBI support.

TGA analysis proofs the thermal stability of the membrane in the intended operational temperature range of 150–190 °C. More importantly, the PBI/IL membrane outperforms Nafion® 117 in terms of fuel cell performance at temperatures above 95 °C. At 150 °C a power density of 0.039 W cm^{-2} is observed, which proofs that the developed PBI/IL membrane can be considered a serious candidate for high temperature fuel cell applications.

References

[1] A.J. Appleby, Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 354 (1996) 1681–1693.
[2] S.J. Peighambardoust, S. Rowshanzamir, M. Amjadi, International Journal of Hydrogen Energy 35 (2010) 9349–9384.
[3] S. Litster, G. McLean, Journal of Power Sources 130 (2004) 61–76.
[4] K. Jiao, I.E. Alaefour, X. Li, Fuel 90 (2011) 568–582.
[5] Q. Li, J.O. Jensen, R.F. Savinell, N.J. Bjerrum, Progress in Polymer Science (Oxford) 34 (2009) 449–477.
[6] J. Lobato, P. Cañizares, M.A. Rodrigo, J.J. Linares, J.A. Aguilar, Journal of Membrane Science 306 (2007) 47–55.
[7] M. Martinez, Y. Molmeret, L. Cointeaux, C. Iojoiu, J.-C. Leprêtre, N. El Kissi, P. Judeinstein, J.-Y. Sanchez, Journal of Power Sources 195 (2010) 5829–5839.
[8] A. Ainla, D. Brandell, Solid State Ionics 178 (2007) 581–585.
[9] G. Alberti, M. Casciola, L. Massinelli, B. Bauer, Journal of Membrane Science 185 (2001) 73–81.
[10] C. Schmidt, T. Glück, G. Schmidt-Naake, Chemical Engineering and Technology 31 (2008) 13–22.
[11] C.H. Park, C.H. Lee, M.D. Guiver, Y.M. Loo, Progress in Polymer Science 36 (2011) 1443–1498.
[12] T.S. Chung, Journal of Macromolecular Science – Reviews in Macromolecular Chemistry and Physics 37 (1997) 277–301.
[13] E.W. Cloe, Polymer Materials Encyclopedia, CRC Press, New York, 1996.
[14] J.K. Lee, J. Kerres, Journal of Membrane Science 294 (2007) 75–83.
[15] J. Lobato, P. Cañizares, M.A. Rodrigo, J.J. Linares, G. Manjavacas, Journal of Membrane Science 280 (2006) 351–362.
[16] A. Carollo, E. Quartarone, C. Tomasi, P. Mustarelli, F. Belotti, A. Magistris, F. Maestroni, M. Parachini, L. Garlaschelli, P.P. Righetti, Journal of Power Sources 160 (2006) 175–180.
[17] C.-H. Shen, S.L.-C. Hsu, E. Bulycheva, N. Belomoima, Journal of Membrane Science 399-400 (2012) 11–15.
[18] J. Yang, Q. Li, J.O. Jensen, C. Pan, L.N. Cleeman, N.J. Bjerrum, R. He, Journal of Power Sources 205 (2012) 114–121.
[19] J.T.-W. Wang, S.L.-C. Hsu, Electrochimica Acta 56 (2011) 2842–2846.
[20] S. Washiro, M. Yoshizawa, H. Nakajima, H. Ohno, Polymer 45 (2004) 1577–1582.

[21] L.A. Neves, J. Benavente, I.M. Coelhoso, J.G. Crespo, Journal of Membrane Science 347 (2010) 42–52.
[22] H. Ye, J. Huang, J.J. Xu, N.K.A.C. Kodiweera, J.R.P. Jayakody, S.G. Greenbaum, Journal of Power Sources 178 (2008) 651–660.
[23] A.N. Mondal, B.P. Tripathi, V.K. Shahi, Journal of Materials Chemistry 21 (2011) 4117–4124.
[24] T. Yamaguchi, F. Miyata, S.-I. Nakao, Journal of Membrane Science 214 (2003) 283–292.
[25] H.-L. Lin, T.L. Yu, W.-K. Chang, Journal of Power Sources 164 (2007) 481–487.
[26] H.L. Lin, Y.C. Chen, C.C. Li, C.P. Cheng, T.L. Yu, Journal of Power Sources 181 (2008) 228–236.
[27] S.H. Yoo, J.H. Kim, J.Y. Jho, J. Won, Y.S. Kang, Journal of Membrane Science 236 (2004) 203–207.
[28] R.M. Boom, I.M. Wienk, T. Van Den Boomgaard, C.A. Smolders, Journal of Membrane Science 73 (1992) 277–292.
[29] S.R. Reijerkerk, R. Jordana, K. Nijmeijer, M. Wessling, International Journal of Greenhouse Gas Control 5 (2011) 26–36.
[30] M.H. Yildirim, D. Stamatialis, M. Wessling, Journal of Membrane Science 321 (2008) 364–372.